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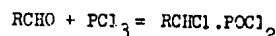
INVESTIGATIONS OF ORGANIC PHOSPHORUS COMPOUNDS. REPORT NO XV:
REACTION OF FORMALDEHYDE WITH PHOSPHORUS TRICHLORIDE

M. I. Kabachnik and Ye. S. Shepeleva
Inst Org Chem, Acad Sci USSR
Submitted 3 Jul 1950

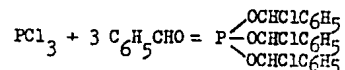
Acid dichlorides of the type described in this report can be used for
the synthesis of analogs of known cholinesterase inhibitors, i.e., nerve
gases.

The reaction of formaldehyde with phosphorus trichloride was investigated.
It was found that at 250° C the acid chloride of chloromethyl phosphonic acid
is formed with a 60 percent yield. A number of derivatives of this acid were
obtained. The secondary and intermediate products of the reaction were in-
vestigated. Their structure confirms the scheme of the reaction of aldehydes
and phosphorus trichloride, which we proposed earlier.

In previous reports [1] we showed that the acid chloride of α -chloro
alkyl phosphonic acid is formed in the reaction of aldehydes with phosphorus
trichloride upon heating to 200° C in sealed tubes and in a molar ratio of 1:1:



We also made the assumption that this reaction goes through the stage of
addition of three aldehyde molecules to the phosphorus trichloride, with the
formation of the corresponding chloro-substituted esters of phosphorous acid,
e.g.:



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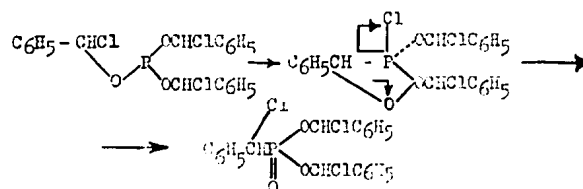
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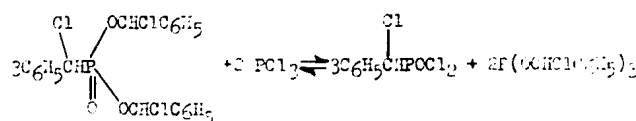
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This compound undergoes an Arbuzov rearrangement under the effect of halogen-substituted alkyl group of its own molecule:



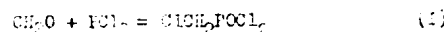
The ester of the α -chloro-substituted acid which is formed reacts with the excess phosphorus trichloride to form the acid chloride of the α -chloro-substituted phosphonic acid and again the same ester of phosphorous acid:



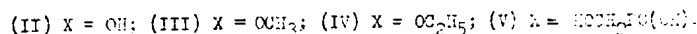
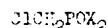
The latter again undergoes an Arbuzov rearrangement, etc., as long as the reaction does not come to an end with a mol-to-mol ratio of the components.

We also stated that the reaction which we found is quite common and can serve for the preparation of various α -halogen-substituted phosphonic acids.

The report below deals with a more detailed investigation of this reaction, under application to the simplest possible aldehyde, i.e., formaldehyde. Since water-free formaldehyde reacts violently with phosphorus trichloride and polymerizes during the reaction, we carried out the reaction with paraformaldehyde, following the example of Page [27]. As in the case of benzaldehyde, paraformaldehyde reacts slowly with phosphorus trichloride, forming a syrup-like mass from which no individual substances can be separated. In distillation, even at a high vacuum, it decomposes, and under no circumstances does it lend itself to crystallization or other purification methods. However, if this syrup-like mass is heated in a sealed tube or in an autoclave to 250° for 5 to 10 hours, it becomes dark, fluid, and can then be distilled over in vacuum, giving a 60 to 65 percent yield of the acid chloride of chloromethyl phosphonic acid (I). The process is expressed by the general equation:



The acid chloride of chloromethyl phosphonic acid contains three chlorine atoms, sharply differing with respect to their reaction properties. The chlorine atoms of the acid chloride are easily hydrolyzed with the formation of chloromethyl phosphonic acid (II):



Pouring into alcohol (methyl or ethyl) converts the acid chloride into the methyl ester (III) or ethyl ester (IV) of chloromethyl phosphonic acid, respectively. On the other hand, the exchange of the third chlorine atom can be brought about only with great difficulty. It cannot be accomplished by boiling with water, nor by heating with water in a sealed tube up to 150-160°C. Only heating with water to 250° C will convert the chloromethyl phosphonic acid to

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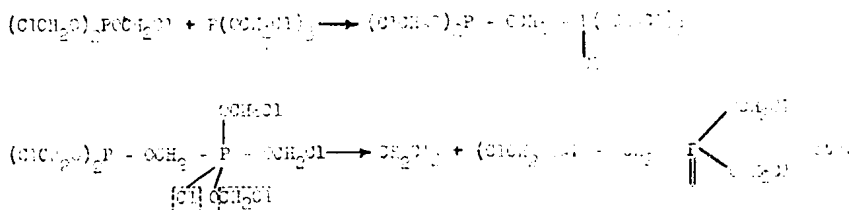
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$$\begin{array}{l}
 \text{PCl}_3 + 3\text{CH}_2\text{O} \longrightarrow \text{P}(\text{OCH}_2\text{Cl})_3 \longleftarrow \\
 \text{P}(\text{OCH}_2\text{Cl})_3 \longrightarrow \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \quad \text{Cl} \end{array} - \text{P}(\text{OCH}_2\text{Cl})_2 \\
 \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \quad \text{Cl} \end{array} - \text{P}(\text{OCH}_2\text{Cl})_2 \longrightarrow \begin{array}{c} \text{ClCH}_2\text{P}(\text{OCH}_2\text{Cl})_2 \\ \parallel \\ \text{O} \end{array} \\
 3\text{ClCH}_2\text{P}(\text{OCH}_2\text{Cl})_2 + 2\text{PCl}_3 \longrightarrow 3\text{ClCH}_2\text{POCl}_2 + 2\text{P}(\text{OCH}_2\text{Cl})_3
 \end{array}
 \quad (\text{I})$$

Above all, we noted the circumstance that the reaction with phosphorus trichloride does not proceed completely in the direction of the formation of acid chloride (II), the yield of which does not exceed 65 percent. In all experiments a nondistilling residue was formed. Its quantity depended on the conditions of the experiment. On the basis of the scheme suggested by us for the fundamental reaction, conclusions can be drawn about the nature of this residue and its formation. It is the result of the incomplete reaction of acid chloride (I). It is possible to draw an analogy between the reactions of phosphorus trichloride with aldehydes and with ethylene oxide. The latter has been studied by Kargin et al. and by P. A. Rodynskaya [2]. An intramolecular rearrangement of the acid chloride β -halogen ester of phosphorus acid is observed in that case. The ester also undergoes an intramolecular Arbuzov rearrangement. Here, too, a nondistillable residue is always left. Its nature has been identified. It is not the result of an intramolecular, but of an intermolecular Arbuzov rearrangement [3]. In the case of the reaction of phosphorus trichloride with formaldehyde, trichloromethyl phosphite is formed originally. It can be eliminated by the Arbuzov method. Intramolecularly (the fundamental direction of the reaction) as well as intermolecularly (formation of the nondistilling residue), e.g.:



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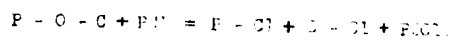
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As a result of this peculiar process of polyalkylation, more or less complex products must be formed, with the structural elements

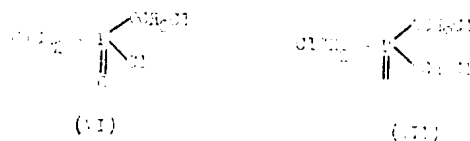


If all this be true, then all P - O - C bonds should be broken up in the action of phosphorus pentachloride on the nondistilling residue, with the formation of the corresponding P - Cl and C - Cl bonds:



As a result, the acid chloride (I) which is already known to us should be formed. The experiment fully confirmed these statements, namely, that in the action of phosphorus pentachloride on the nondistilling residue left from the fundamental reaction, the acid chloride of chloromethyl phosphonic acid is formed smoothly in a quantity of 100 percent of the weight of the residue (in this case, an increase in weight is to be expected; we do not forget the yield, since the initial residue is a complex mixture and not a definite substance).

The second argument in favor of our assumption about the mechanism of the reaction was arrived at in the investigation of the products of the reaction of paraformaldehyde with phosphorus trichloride in a ratio other than 1:1, e.g., 2:1. In this case, the reaction does not proceed smoothly. A large quantity of nondistilling residue is formed, and the yield of acid chloride (I) is considerably lower. Nevertheless, by distilling the reaction products, it is possible here to separate the higher fractions which, according to data of the analysis, correspond to the chloromethyl esters of chloromethyl phosphonic acid of constitution (VI) and (VII):



The forming of these substances in the presence of an excess of formaldehyde (insufficient quantity of phosphorus trichloride, full carrying out of the reaction) can be suggested.

Reaction of Phosphorus Trichloride with Paraformaldehyde

The reaction of phosphorus trichloride with paraformaldehyde proceeds slowly in the cold. A syrup is formed in this reaction. Individual substances cannot be separated directly from this syrup. On being heated in a sealed tube or in a retort, the syrup undergoes a change. It becomes more fluid. It can then be distilled over in vacuum. After two or three distillations it breaks down into a main fraction, boiling at 75-77° C at 0.5 mm or at 81-85° C at 13 mm, representing the acid chloride of chloromethyl phosphonic acid (I), a small fraction boiling around 100° C at 0.5 mm or at 120° C at 13 mm, which is the acid dichloride (II), and a very insignificant fraction boiling at 130° C at 1 mm, the ester (VII). The yield of acid chloride (I) varied, depending on the ratio between the components of the reaction, the temperature, and the duration of the distillations. In all experiments, a nondistilling residue was left, sometimes in considerable quantity. The quantity increased as the yield decreased.

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1. Five gr of lry paraformaldehyde (0.167 mols) and 35 gr of phosphorus trichloride (0.250 mols) were heated for 10 hr in a sealed tube at 235-245° C. From the reaction product, the phosphorus trichloride was first distilled off in a low vacuum, and the residue was then distilled in vacuum. After two distillations, 17.1 gr (61 percent) of acid chloride (I) were obtained (bp 84-85° C at 13 mm, n_D^{20} 1.4990); residue 1.1 gr.

2. Five gr of paraformaldehyde (0.167 mols) and 23.7 gr of phosphorus trichloride (0.172 mols) were heated for 2 hr at 180-200° C. After three distillations, 4.5 gr (16 percent) of acid chloride (I) were obtained, with a boiling point of 87-88° C at 15 mm (n_D^{20} 1.4978; d_4^{20} 1.6361). In addition, 1.5 gr of an intermediate fraction with a boiling point of 95-120° C at 15 mm and 0.5 gr (1.5 percent) of product (VI) with a boiling point of 120° at 15 mm (n_D^{20} 1.4949) were obtained. The residue was 4.5 gr.

3. Five gr of paraformaldehyde (0.167 mols) and 7.9 gr phosphorus trichloride (0.057 mols) were heated for 2 hr at 190-210° C. After 3 distillations, a total of 1 gr (4 percent) of acid chloride (I) with a boiling point of 52° C at 2 mm and n_D^{20} 1.4980, and also a small intermediate fraction as well as 0.4 gr of product (VI) with a boiling point of 96-99° C at 2 mm (n_D^{20} 1.4920) resulted. The nondistilling residue weighed 6.8 gr.

4. Thirty gr of paraformaldehyde (1 mol) and 72 gr of phosphorus trichloride (0.5 mols + 5 percent) were heated for 2 hr to 160-180° C. After several distillations, 17 gr (10 percent) of product (I), 2 gr (1 percent) of product (VI), and 0.2 gr of product (VII) (boiling point 120° C at 2 mm; n_D^{20} 1.4870) were obtained.

5. For obtaining large quantities of acid chloride (I), the experiment was carried out in an autoclave under the conditions of Experiment 1. With a charge of 1 gram-mol of paraformaldehyde and 1.5 gram-mols of phosphorus trichloride, 0.6 mols of acid chloride (I) were obtained. The acid chloride can easily be prepared in any quantity by this method.

Acid Chloride of Chloromethyl Phosphonic Acid (I). This substance is a colorless, mobile liquid, which fumes slightly in air. It is insoluble in water, but reacts quickly with it under evolution of heat. Boiling point 87-88° C at 15 mm, 84-85° C at 13 mm, 78-79° C at 10 mm, 52-53° C at 2 mm; n_D^{20} 1.4978; d_4^{20} 1.6361; MR: 30.00; MR (calculated): 29.74.

Percentage of phosphorus found: 18.01, 18.25

Percentage of phosphorus calculated in CH_2OPCl_3 : 18.52

Acid Chloride of The Monochloromethyl Ester of Chloromethyl Phosphonic Acid (VI). Colorless liquid, fuming in air, soluble in water. Boiling point 84-85° C at 1 mm, 99-101° C at 2 mm, 120° C at 15 mm; d_4^{20} 1.6082; n_D^{20} 1.4942; MR: 35.86; MR (calculated): 35.63.

Percentages found: C:12.15; H:2.11; P:16.02, 15.58

$C_2H_4O_2PCl_3$ percentages calculated: C:12.15; H:2.02; P:15.70

On repeated distillation, the substance decomposes, splitting off formaldehyde.

Dichloromethyl Ester of Chloromethyl Phosphonic Acid (VII). A colorless liquid which does not fume in air. Boiling point 120° C at 2 mm; n_D^{20} 1.4870.

Percentage of phosphorus found: 12.93, 13.13

Percentage of phosphorus calculated in $C_3H_6O_3PCl_3$: 13.60

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Because of the small quantity of the substance obtained in the reaction, more detailed characteristics cannot be given.

Obtaining of Acid Chloride of Chloromethyl Phosphonic Acid From the Nondistilling Residue

20.5 gr of phosphorus pentachloride were added to the 5.8 gr of nondistilling residue left from the distillation of the products of the reaction between paraformaldehyde and phosphorus trichloride. The reaction proceeded violently at first, but at the end heating on a water bath was required to dissolve the last portions of phosphorus pentachloride. 9.5 gr of phosphorus oxychloride were obtained, which were driven off at 38-42° C and 66 mm (in this process, a part of the oxychloride did not condense). 7.0 gr of acid chloride (I) with a boiling point of 84-86° C were obtained. The residue (carbonaceous substances) was 1.0 gr.

Methyl Ester of Chloromethyl Phosphonic Acid (III)

Five gr of acid chloride (I) were mixed under strong cooling (using a cooling mixture) with 15 gr of absolute methyl alcohol and the mixture was left to stand overnight. Then the alcohol was distilled off in vacuum, and the residue was distilled. After two distillations, 2.5 gr of methyl ester of chloromethyl phosphonic acid were obtained. It boiled at 59-60° C at 1 mm. n_D^{20} :1.4425; d_4^{20} :1.3283; MR: 31.60; MR (calculated):31.78. It is a colorless liquid.

Percentages found: C:22.41, 22.43; H:5.02, 4.95

$C_2H_5O_3PCl$ percentages calculated: C:22.71; H:5.09

Ethyl Ester of Chloromethyl Phosphonic Acid (IV)

Prepared similarly to the preceding substance, 3 gr of ethyl ester of chloromethyl phosphonic acid were obtained from 5 gr of acid chloride (I) and 15 gr of absolute ethyl alcohol after two distillations. The substance boiled at 80-81° C at 2 mm. In carrying out the synthesis on a large scale, a yield reaching 72 percent was obtained. A colorless liquid, soluble in water and easily soluble in alcohol. Boiling point 101° C at 5 mm; n_D^{20} :1.4415; d_4^{20} :1.1992; MR:41.12; MR (calculated) 41.02.

Percentages found: C:32.03, 32.18; H:6.23, 6.19

$C_4H_{12}O_3PCl$ percentages calculated: C:32.17, H:6.54

Chloromethyl Phosphonic Acid (II)

The acid chloride of chloromethyl phosphonic acid (I) fumes in air. It is hygroscopic and forms a homogeneous solution. When it is placed in a desiccator over sulfuric acid, it gradually crystallizes in large needles. However, on recrystallizing the substance obtained in this manner, it is difficult to reach a sharply defined melting point (possibly because of the formation of anhydrides). The acid was obtained in the pure form in experiments in which attempts to saponify the third chlorine atom by heating with water were made.

Five gr of acid chloride (I) were added, drop by drop, to 15 ml of water. The mixture was then evaporated on a water bath. The HCl was removed by evaporation with water and alcohol. The residue was left in the desiccator over sodium hydroxide. After drying (4 gr), it was twice recrystallized from a mixture of ether and toluene with gradual evaporation of the solvent in a

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desiccator over paraffin and sulfuric acid. The boiling point was 86-87.5° C. The substance is soluble in water, alcohol, glacial acetic acid, ethyl acetate, and ether. It is insoluble in benzene, petroleum ether, and dichloroethane; however, it is difficult to precipitate it with these solvents.

Percentages found: C:9.27, 9.33; H:3.03, 3.03

CH₄O₃PCl percentages calculated: C:9.20; H:3.06

Oxymethyl Phosphonic Acid From Chloromethyl Phosphonic Acid

0.8 gr of chloromethyl phosphonic acid and 10 ml of water were heated in a sealed tube for 2 hr to 250° C. The syrup which remained after evaporation of the solution was placed in a desiccator over phosphorus pentoxide. It crystallized within 2 days. The substance was recrystallized by dissolving it in a minimum quantity of absolute alcohol and adding ethyl acetate. The substance crystallized out on evaporation of the solvent over sulfuric acid and paraffin. The melting point was 98-99° C; the melting point of a mixed sample with oxymethyl phosphonic acid prepared according to Page's method ^[2] and recrystallized by the same method (melting point 99-100.5° C) was 98-100° C. The melting point of a mixed sample with the initial chloromethyl phosphonic acid was 64-65° C. Thus, oxymethyl phosphonic acid, obtained from chloromethyl phosphonic acid, is identical to that prepared according to Page's method.

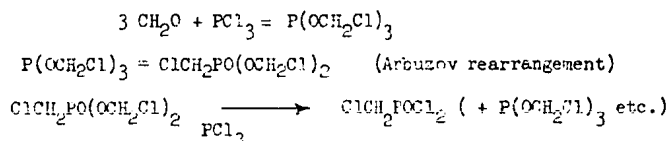
The analysis of the oxymethyl phosphonic acid prepared from chloromethyl phosphonic acid is as follows:

Percentages found: C:10.43, 10.47; H:4.07, 4.30

CH₅O₄P percentages calculated: C:10.71; H:4.46

Summary

1. Phosphorus trichloride reacts with formaldehyde, forming the acid chloride of chloromethyl phosphonic acid ClCH₂POCl₂.
2. The constitution of the acid chloride of chloromethyl phosphonic acid is indicated by its conversion into the chloro-acid ClCH₂PO(OH)₂ and further into the oxy-acid OHCH₂PO(OH)₂.
3. ClCH₂PO(OR)₂ esters of chloromethyl phosphonic acid were obtained.
4. The proposed mechanism of the reaction of formaldehyde with phosphorus trichloride is as follows:



5. In confirmation of the proposed mechanism of the reaction, ClCH₂PO(OCH₂Cl)₂ and ClCH₂PO(OCH₂Cl)Cl were isolated from the reaction mixture, in addition to ClCH₂POCl₂.

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